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**MEMBRANE-BASED FUEL  
DEOXYGENATION FOR COKE  
SUPPRESSION**

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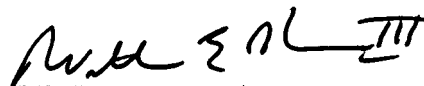
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14. ABSTRACT (Maximum 200 Words) A prototype membrane module for on-line removal of dissolved oxygen, that would otherwise react to form coke precursors, was constructed and successfully demonstrated. Fuel flows over the polymer membrane, while oxygen diffuses through it at a rate that is proportional to the difference in oxygen partial pressures across the surface. Tests were conducted with membranes of different thickness, and over a range of fuel flow rates (residence times) and temperatures. The membrane was shown to be capable of removing essentially all of the dissolved oxygen (to <1 ppm). Fuel deoxygenation proved to be very effective in suppressing autoxidative coke formation, making it possible to increase the maximum allowable temperature and more than double the available heat sink. Moreover, deoxygenated Jet A was shown to perform as well as JP-7, the Air Force's highest thermal stability fuel. An analytical model for oxygen permeation through the membrane was formulated, and used in conjunction with the test data to show that practical size (i.e., low-volume/high-flowrate) deoxygenators can be designed for use in aircraft systems.					
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## TABLE OF CONTENTS

<b><u>Section</u></b>	<b><u>Page</u></b>
LIST OF FIGURES.....	iv
LIST OF TABLES.....	v
FOREWORD .....	vi
1. SUMMARY .....	1
2. INTRODUCTION.....	2
3. EXPERIMENTAL APPROACH .....	4
4. CONCEPT DEMONSTRATION .....	9
5. MODELING .....	13
6. SYSTEM DESIGN/DEVELOPMENT .....	16
7. CONCLUSION.....	17
8. REFERENCES .....	18

## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
1. Supported Oxygen-Permeable Membrane .....	3
2. Membrane Test Apparatus .....	4
3. Influence of Oxygen Temperature on Membrane Permeability .....	5
4. Influence of Membrane Thickness on Oxygen Permeability.....	6
5. Influence of Fuel Temperature on Deoxygenation.....	7
6. Influence of Mass Diffusion in Fuel on Deoxygenation .....	8
7. Demonstration of Single-Pass Fuel Deoxygenation.....	9
8. Deoxygenation Suppresses Coke Formation, Independent of Fuel ....	11
9. Deoxygenation is Effective up to 860 F Wall Temperature .....	12
10. Deoxygenated Fuel Performs As Well As JP-7 .....	12
11. Kinetic Model Validation.....	14
12. Fuel Deoxygenation Filter Sizing .....	15
13. Fuel Deoxygenator Design Concept.....	16

## LIST OF TABLES

<b><u>Table</u></b>	<b><u>Page</u></b>
1. Jet Fuel Thermal Oxidation Tests.....	10

## **1. FOREWORD**

This report summarizes work performed for the Air Force Research Laboratory, Propulsion Directorate under Delivery Order 3 of Contract F33615-97-D-2784, and on research supported by the United Technologies Corporation. Dr. Tim Edwards of the AFRL Turbine Engine Division, Fuels Branch, administered the Air Force contract, and the Program Manager at UTRC was Dr. Louis J. Spadaccini. The authors gratefully acknowledge the test support provided by Mr. David McHugh.

## 1. SUMMARY

Fuel deoxygenation is being developed as a means for suppressing autoxidative coke formation in aircraft fuel systems, thereby increasing the exploitable cooling capacity of the fuel, enabling major increases in engine operating temperature and cycle efficiency. Reduced maintenance is an added benefit. A prototype membrane filter module for on-line removal of dissolved oxygen, which would otherwise react to form coke precursors, was constructed and successfully demonstrated. The fuel flows over the membrane, while oxygen diffuses through it at a rate that is proportional to the difference in oxygen partial pressures across the surface. Tests were conducted over a range of fuel flow rates (residence times) and temperatures. The filter was operated with air-saturated jet fuel for several hours at a steady-state condition, verifying the capability to remove essentially all of the dissolved oxygen (to <1 ppm) and proving the viability of the concept.

A convincing demonstration of coke suppression was performed when air-saturated (normal) and deoxygenated jet fuels were tested in a standard ASTM heated tube apparatus at wall temperatures as high as 850 F. With deoxygenated fuel, there was a dramatic reduction (more than an order of magnitude) in coke deposition relative to air-saturated Jet A, which will allow the maximum fuel temperature to be increased by more than 200 F, doubling the available heat sink. Moreover, deoxygenated Jet A was shown to perform as well as JP-7, the Air Force's highest thermal stability fuel. An analytical model for oxygen permeation through the membrane was formulated, and used in conjunction with the test data to estimate the filter size required for a practical (i.e., low-volume/high-flowrate) deoxygenator.



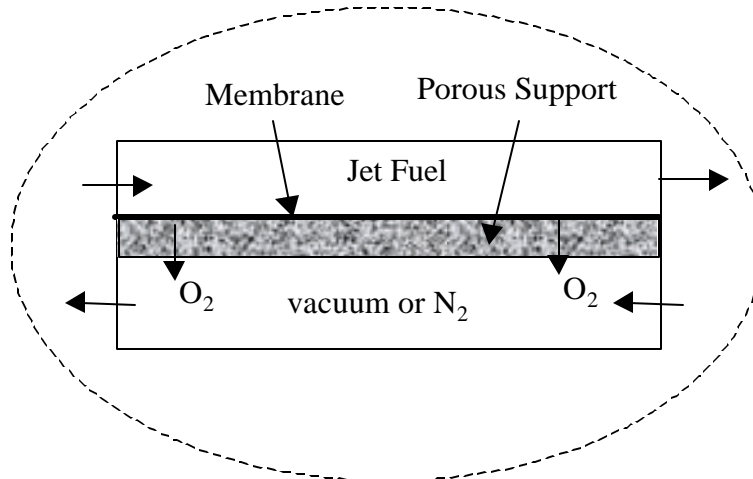
## 2. INTRODUCTION

Thermal management is a design driver for advanced gas turbine engines. Increasing cycle temperature increases engine performance and cycle efficiency. However, improved materials for enabling high-temperature operation are not available. Fuel is currently used as a heat sink for the engine oil system, but its cooling capacity is limited by a temperature constraint necessary to preclude the formation of coke deposits. Therefore, it is essential to develop a method to suppress coke formation and, thereby, significantly increase the available heat sink and permit extended utilization of the fuel for component and system cooling (e.g., turbine, compressor, and avionics) in advanced engines and sustained flight at high Mach number. Over the past 40 years there have been many attempts by researchers to suppress coking [1,2], but, with the exception of JP-8+100 additives [3] that allow operation up to 425 F, they have proven to be unsuccessful or impractical.

The major factor contributing to coke deposition at temperatures up to approximately 700 F is oxygen that dissolves into the fuel when it comes in contact with air [4]. When air-saturated fuel is heated above approximately 300 F, the dissolved oxygen reacts to form free-radical species (coke precursors) that initiate and propagate other autoxidation reactions, leading to deposit formation. These reaction paths become insignificant when the concentration of the dissolved oxygen is reduced from its ambient saturation level of 70 ppm to approximately 1 ppm (i.e., deoxygenated) [1]. At temperatures above approximately 900 F, the deposition mechanism is characterized by pyrolysis, wherein chemical bonds are broken and large alkanes are converted into smaller alkanes, alkenes, and some hydrogen [5]. Since pyrolysis requires much higher temperatures than autoxidation, reducing the oxygen content of fuel will allow it to be heated significantly before thermal decomposition begins, increasing the cooling capacity. Therefore, fuel deoxygenation should dramatically reduce autoxidative coke deposition, and make it possible to realize the thermal stability goals for JP-8+225/JP-900 [6].

This study deals with the development of a small, practical membrane-based filter for on-line removal of dissolved oxygen that would otherwise react and form the precursors for autoxidative coke. A permeable membrane is a selective barrier that permits the separation of certain species in a fluid by diffusion or sorption-diffusion mechanisms. In general, the membrane structure consists of an ultra-thin coating that has the requisite separation properties, and a micro-porous polymer support that provides strength. In the present representation (see Figure 1), the oxygen molecules in jet fuel dissolve into the membrane and then diffuse across it, driven by the difference of oxygen partial pressure (chemical potential or driving force), while the hydrocarbon molecules are unaffected and pass over it. Previous attempts at deoxygenating fuel have included sparging with nitrogen, and the use of molecular-sieve adsorbents and chemical reducing agents. These approaches have proven impractical for aircraft applications because they are costly, heavy and bulky, or even dangerous [7]. Some aircraft use an on-board inert gas generator system (OBIGGS) to reduce the oxygen

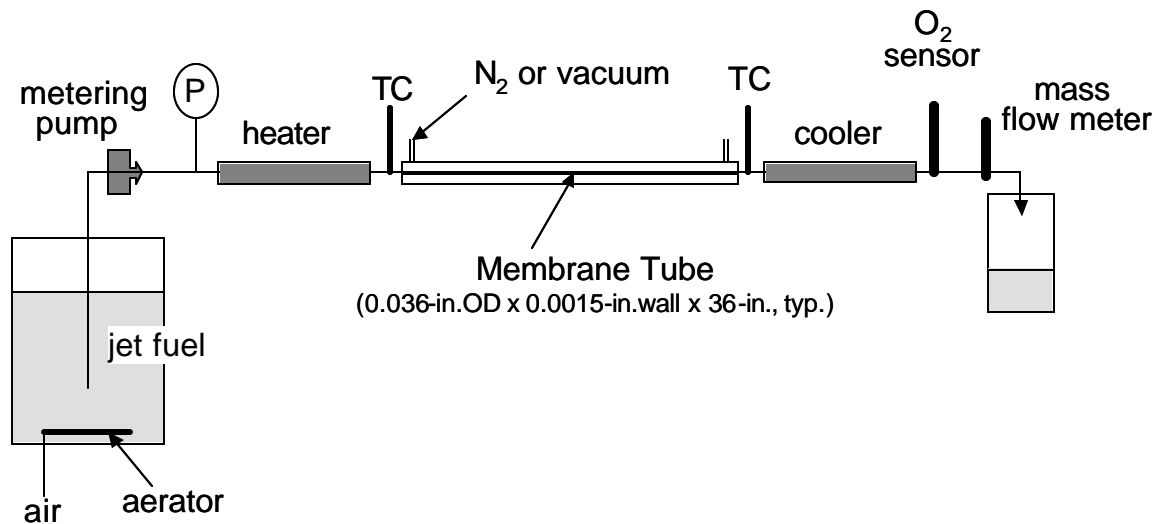
concentration in the fuel tank below the flammability limit (~9 vol. %). However, it is unlikely that a similar system could be used to lower the oxygen concentration dissolved in the fuel to approximately 1 ppm.



**Figure 1: Supported Oxygen-Permeable Polymer Membrane**

### 3. EXPERIMENTAL APPROACH

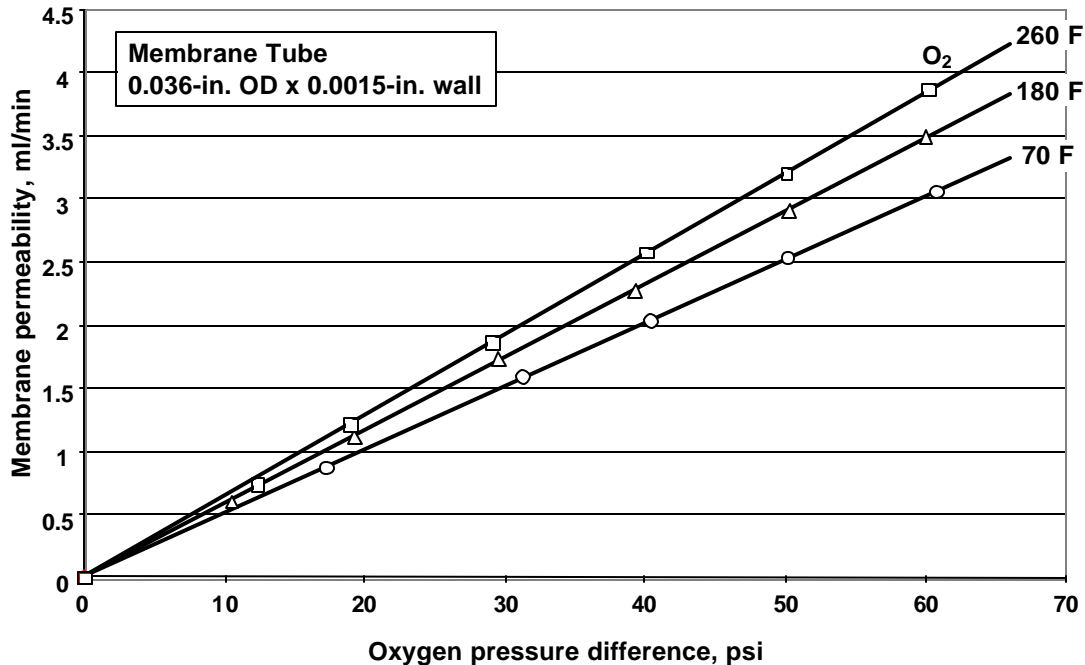
An experimental apparatus for measuring the oxygen removal rate from jet fuel by membrane permeation has been developed and is illustrated schematically in Figure 2. The rig consists of a fuel aeration system, a fuel pump, a preheater, a membrane module, and an on-line oxygen sensor. Although the membrane is envisioned as being very thin to facilitate gas diffusion (e.g., micron thickness), for convenience, concept feasibility experiments were conducted using several closely sized commercially available thin-wall tubes made of the membrane material.



**Figure 2: Membrane Test Apparatus**

In a fuel deoxygenation test, air-saturated jet fuel was metered through the membrane module at a predetermined and controllable pressure, temperature, and flowrate. After leaving the module, the fuel was cooled to ambient temperature (to eliminate measurement uncertainties) and the oxygen concentration determined on-line using a polarographic-type oxygen sensor. The membrane module consisted of a polymeric membrane tube (through which the fuel flowed) installed in a cylindrical shell that was either evacuated or purged with nitrogen, to provide the driving force (oxygen partial pressure difference) for oxygen removal. Tests were conducted in a single-pass flow arrangement over a range of fuel flow rates (residence times) and temperatures. The maximum fuel temperature was limited to 240 F to preclude oxygen depletion due to thermal reactions. This behavior was verified by substituting a stainless-steel tube for the membrane tube and demonstrating that at 240 F the oxygen concentration at the outlet was unchanged from the inlet (i.e., 100% saturated). To verify the oxygen sensor accuracy/repeatability after each test, the fuel was re-aerated to demonstrate measurement of 100 percent saturation.

An initial series of tests was conducted to measure the permeability of a 0.036-in.- OD x 0.0015-in.-wall membrane tube to gaseous oxygen. The

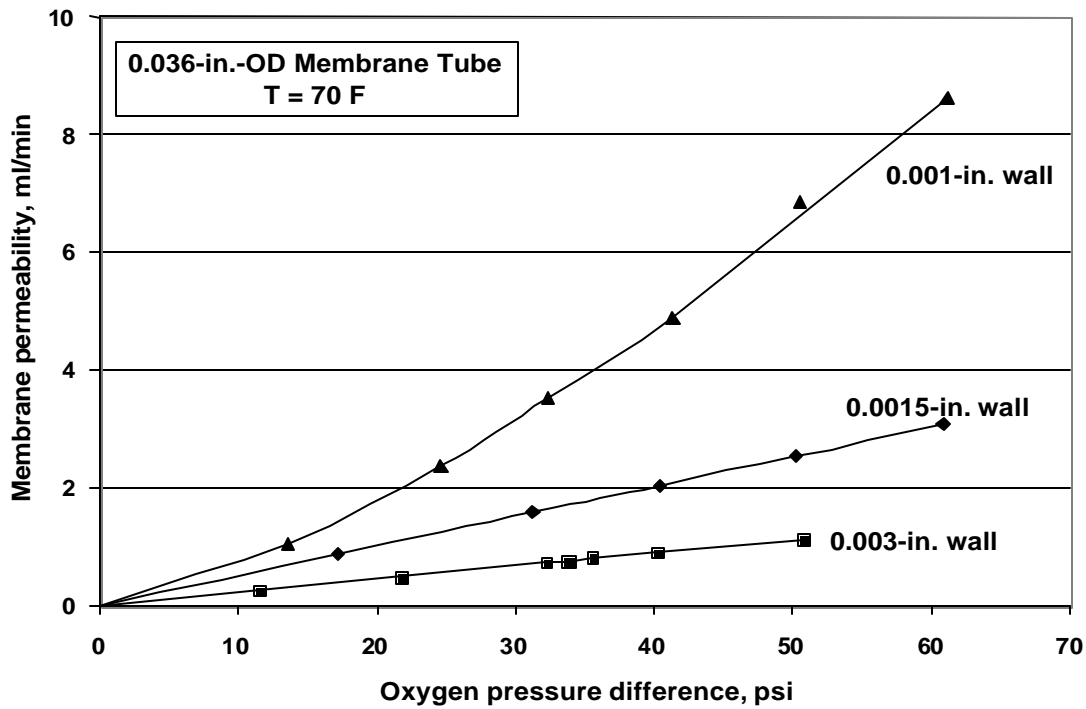


**Figure 3: Influence of Oxygen Temperature on Membrane Permeability**

membrane is essentially impermeable to liquids and organic vapors, and the gas permeability increases as the size of the molecule decreases. The oxygen permeability of the membrane was determined by pressurizing the tube with oxygen, and measuring the amount of gas that diffused through the tube wall into the outer shell. Oxygen permeation rates were determined using bubble-type flowmeters for measuring very low flow rates. The pressure and temperature of the oxygen feed were varied, and the outer shell was maintained at atmospheric pressure. The feed and permeate sides of the module were purged with oxygen prior to each permeation test. The results are presented in Figure 3, and show that the oxygen permeability of the polymer membrane tube increases linearly with the oxygen pressure difference across it, and also increases significantly with increasing temperature.

Another important factor that will influence the oxygen removal rate is the membrane thickness. Additional oxygen-gas permeability tests were conducted to evaluate the effect of membrane thickness using membrane tubing with wall thickness of 0.001-in. and 0.003-in. The results, shown in Figure 4, for ambient temperature (70 F) indicate that the oxygen gas diffusion through the membrane increases rapidly (nearly exponentially) with decreasing thickness, and emphasizes the desirability of the membrane being relatively thin.

The influence of fuel temperature on the rate of oxygen removal is shown in Figure 5 for a 0.003-in.-thick membrane tube. At ambient temperature, the oxygen concentration in air-saturated JP-8 fuel was reduced by 70 percent (to approximately 20 ppm) in a single pass through the 3-ft-long, 0.040-in.-OD polymeric membrane tube. At a fuel temperature of 240 F (a typical aircraft main



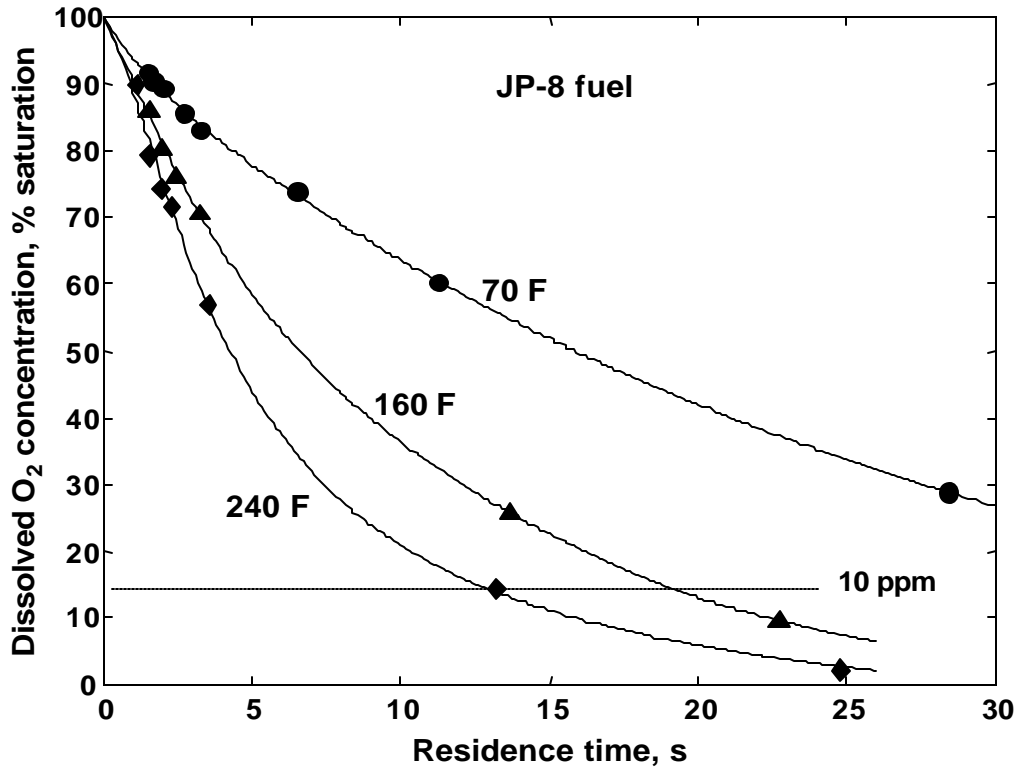
**Figure 4: Influence of Membrane Thickness on Oxygen Permeability**

fuel pump outlet temperature), more than 90 percent of the dissolved oxygen was removed for the same residence time (volume flowrate). That is, the oxygen concentration was reduced from approximately 70 ppm to a level below 5 ppm in a residence time of 25 seconds. This rate of deoxygenation corresponds to a space velocity of 145/hr, where

$$SV = \frac{\text{volume flowrate}}{\text{reactor volume}} = \frac{1}{\text{residence time}} \quad (1)$$

In an aircraft fuel system, higher space velocities will be required to minimize the filter volume. Reducing the membrane thickness and increasing the surface area will enhance oxygen diffusion and facilitate operation at much higher space velocity. Fuel heating enhances performance by increasing the permeability of the membrane, and by decreasing the solubility of oxygen in fuel, thereby increasing the driving force across the membrane. Increasing the pressure of the air-saturated fuel will not produce a significant benefit because it will not change the oxygen partial pressure (which is established in the tank) or significantly increase the permeability of the membrane.

Diffusion of the oxygen molecules dissolved in liquid fuel to the membrane surface can be the rate-determining or rate-limiting step in the fuel deoxygenation process, depending on the oxygen diffusion rate through the membrane. When an effective and thin membrane is used, the overall deoxygenation rate may be

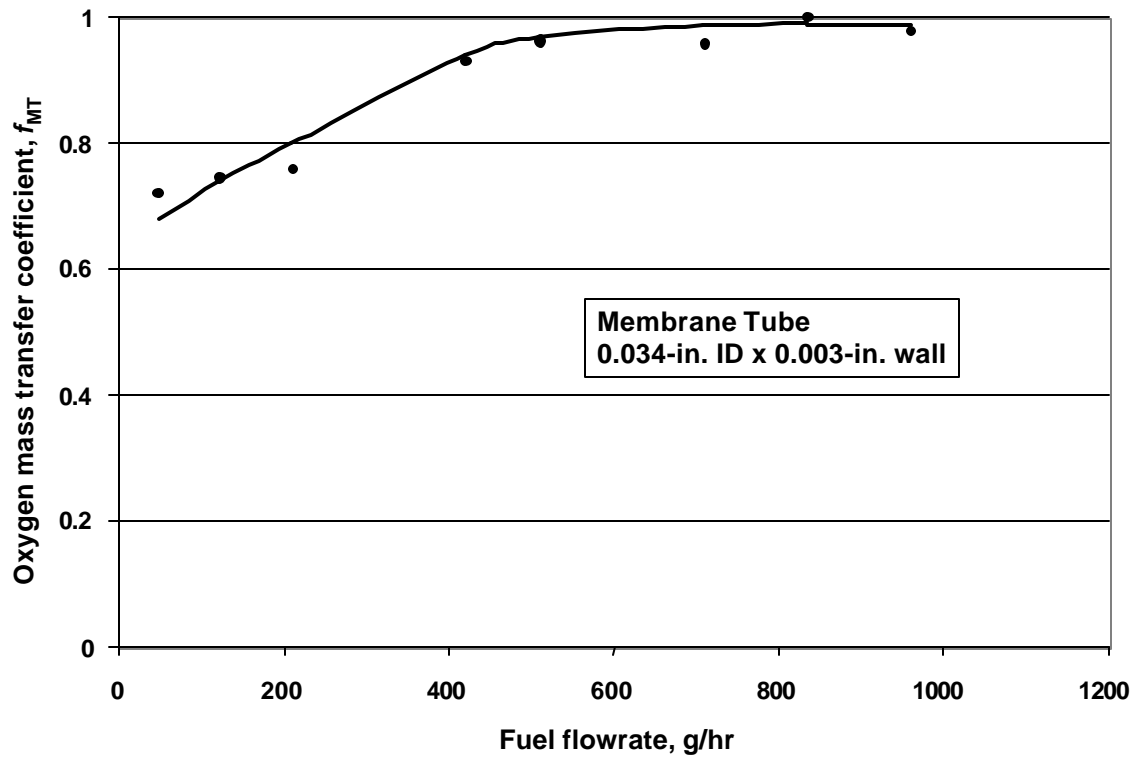


**Figure 5: Influence of Fuel Temperature on Deoxygenation**

controlled by the bulk diffusion of the oxygen molecules in fuel. This effect can be quantitatively described by the oxygen mass transfer coefficient,

$$f_{MT} = \frac{\text{overall oxygen removal rate}}{\text{oxygen diffusion rate through membrane}} \quad (2)$$

where the oxygen diffusion through the membrane is determined from the gas permeability tests discussed above. Mass transfer coefficients for flow in a 0.034-in.-ID x 0.003-in.-wall membrane tube are shown in Figure 6, as a function of the fuel flowrate. The results indicate that the mass transfer coefficient increases as the fuel flowrate increases from 50 g/hr ( $Re = 16$ ) to about 800 g/hr ( $Re = 260$ ). Although the flow is still laminar at 800 g/hr, the bulk diffusion rate of the oxygen molecules in fuel is much faster than the rate through the membrane and, therefore, the mass transfer coefficient approaches 1.0, indicating that there was no limitation caused by mass transfer. Mass transfer in the fuel did limit the overall deoxygenation rate when the fuel flowrate was less than 800 g/hr (i.e.,  $Re < 260$ ).



**Figure 6: Influence of Mass Diffusion in Fuel on Deoxygenation**

#### 4. CONCEPT DEMONSTRATION

A prototype fuel deoxygenator module was constructed for measuring the oxygen removal rate from jet fuel, and tests were conducted over a range of fuel flow rates (residence times) and temperatures. The module consists of a spool of 0.040-in.-ID x 0.003-in.-wall oxygen-permeable membrane tubing installed in a cylindrical container. The container is purged with a low flowrate of nitrogen to create an oxygen-free atmosphere around the tube. Fuel flows inside the tubing, while the dissolved oxygen diffuses through the wall at a rate that is proportional to the difference in the oxygen partial pressures (driving force) across the surface.

Several tests were performed to demonstrate the capability to deoxygenate air-saturated JP-8 fuel to very low concentration levels (<1 ppm) in a single-pass on-line flow arrangement. The tests were conducted with aerated fuel at ambient temperature, a much more difficult condition than occurs in an aircraft fuel system. (In Figure 5, it was shown that the deoxygenation rate increases with

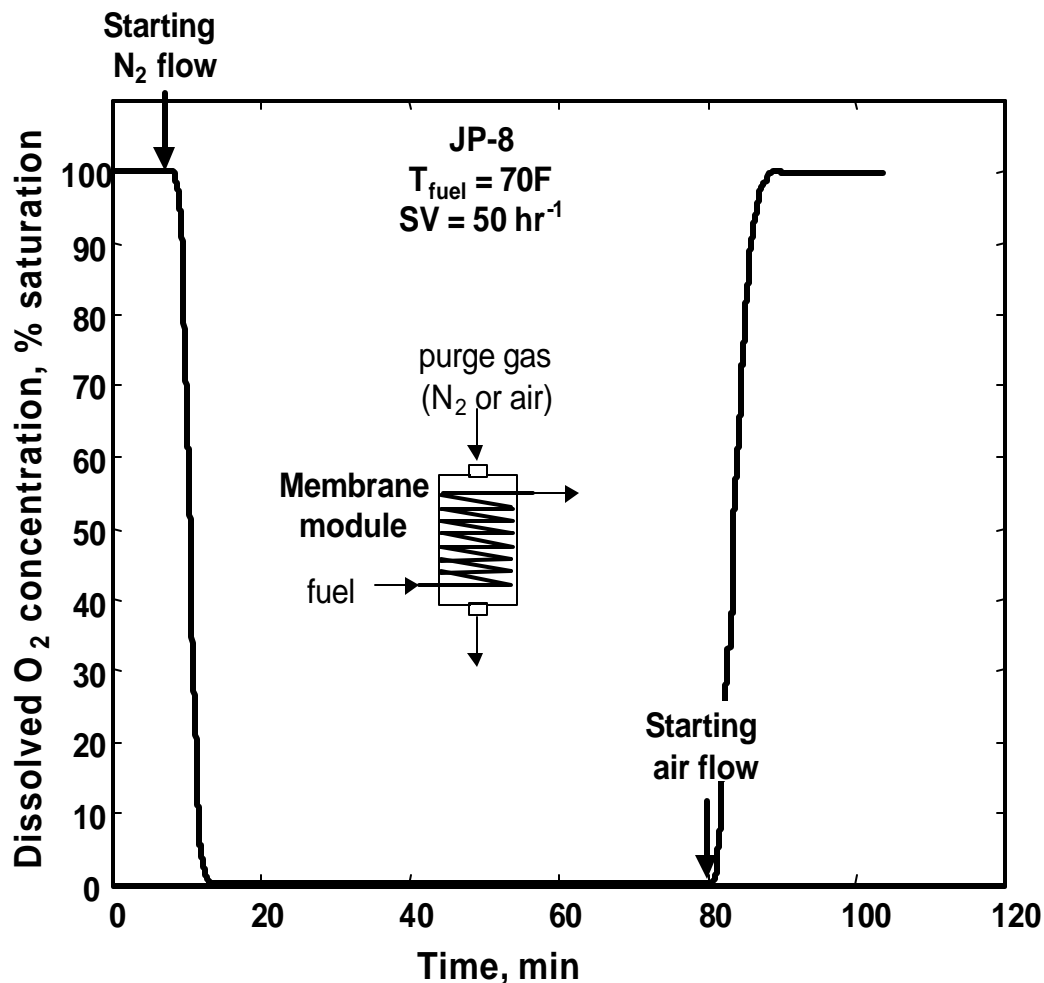


Figure 7: Demonstration of Single-Pass Fuel Deoxygenation



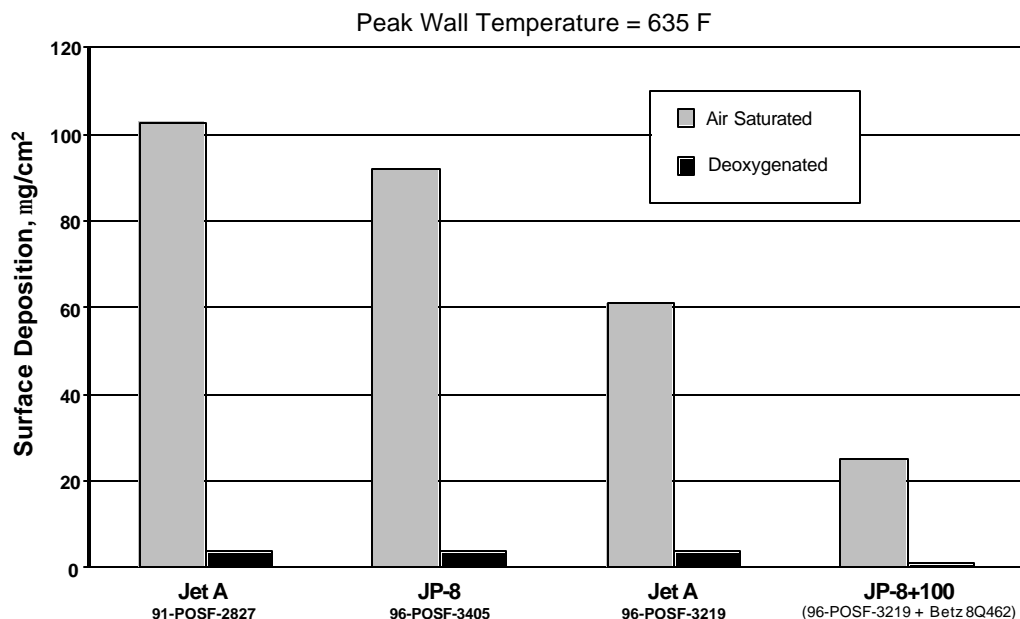
increasing temperature.) Typical results, shown in Figure 7, verify the rapid removal of essentially all of the dissolved oxygen from the fuel, beginning shortly after initiating the nitrogen purge gas flow. The fuel deoxygenator module was operated at a steady-state condition for more than one hour before terminating the nitrogen bleed and initiating an air purge, thereby ending the deoxygenation process (as indicated by the return of the oxygen sensor to the air-saturated-fuel starting condition). This result clearly demonstrates the feasibility of the on-line deoxygenation concept. The fuel pressure loss through the membrane filter can be minimized in a practical design by interchanging the fuel and nitrogen flows, with the fuel being directed over and around a bundle of membrane tubes (enhancing mass transport) and oxygen permeating into the tubes. A candidate design is described below.

To provide a simple demonstration of coke suppression by on-line fuel deoxygenation, a small-scale test apparatus was constructed and tests were performed with typical jet fuels. The fuel deoxygenator module was used in conjunction with an ALCOR Hot Liquid Process Simulator (HLPS) to carry out a series of standard ASTM Jet Fuel Thermal Oxidation Stability Tests (JFTOT Procedure, ASTM Standard Method D 3241). The JFTOT is a pass-fail tester for specification purposes, and not a precision instrument for rating small differences in carbon deposition among fuels. It is used here to reveal potentially large differences in coke formation resulting from fuel deoxygenation.

**Table 1: Jet Fuel Thermal Oxidation Tests**

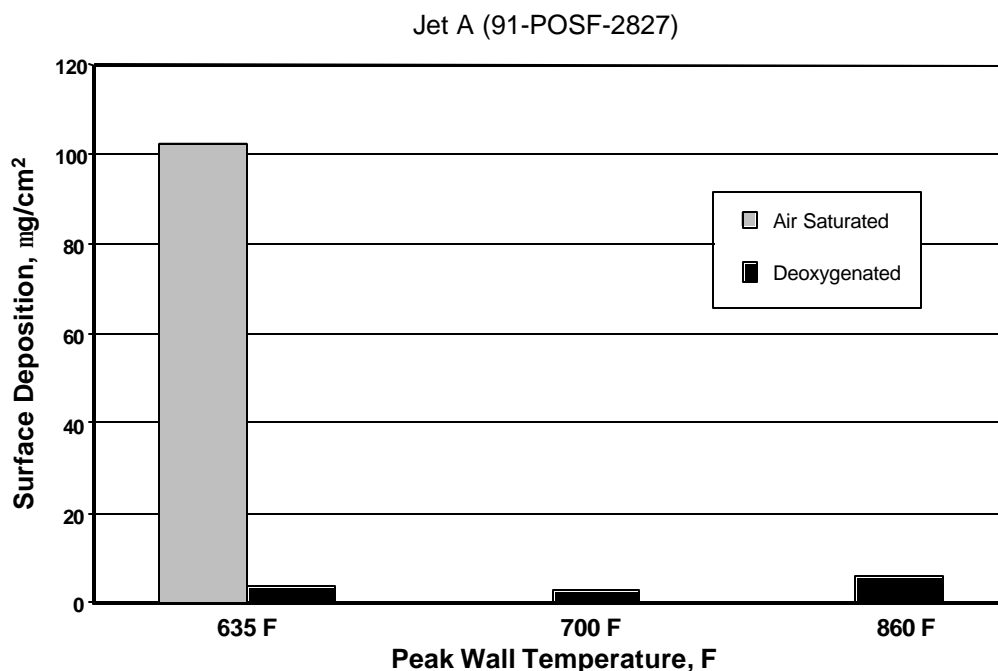
Fuel	Running Mode	Peak Wall Temperature	Surface Carbon	Pressure Drop across Filter
		F	$\mu\text{g}/\text{cm}^2$	mm-Hg/min.
Jet-A <sup>*</sup>	Air-saturated	635	103	240/105
Jet-A <sup>*</sup>	Deoxygenated	635	4	0/300
Jet-A <sup>*</sup>	Deoxygenated	700	3	1/300
Jet-A <sup>*</sup>	Deoxygenated	860	6	12/300
Jet-A <sup>**</sup>	Air-saturated	635	61	240/160
Jet-A <sup>**</sup>	Deoxygenated	635	4	0/300
JP-8	Air-saturated	635	92	1/300
JP-8	Deoxygenated	700	4	0/300
JP-7	Air-saturated	700	5	0/300
JP-7	Air-saturated	840	4	1/300
JP-8+100	Air-saturated	635	25	0/300
JP-8+100	Deoxygenated	635	1	0/300
<sup>*</sup> 91-POSF-2827				
<sup>**</sup> 96-POSF-3219				

Heated-tube JFTOT-Procedure tests were conducted with air-saturated fuel (baseline) and fuels deoxygenated on-line using the membrane module. The dissolved oxygen concentration was monitored continuously and observed to remain constant at either the saturation or near zero level (shown in Figure 7). Because the tube is heated resistively (i.e., by an electrical current), the axial temperature profile is very steep. Type 316 stainless steel tubes were substituted for conventional aluminum tubes to permit operation at high temperatures and quantification of the surface deposit by carbon burn-off using a LECO RC-412 Carbon Determinator (precision of  $\pm 2\%$ ). Evaluations were performed with Jet A, JP-8, and JP-7 in 5-hour tests at maximum tube temperatures of 635-860 F and fuel flow rate of 3 ml/min, conditions that are much more severe than the normal JFTOT Procedure. These fuels and run conditions were used previously in the development program for JP-8+100, and an extensive database is available for comparison of results [8].



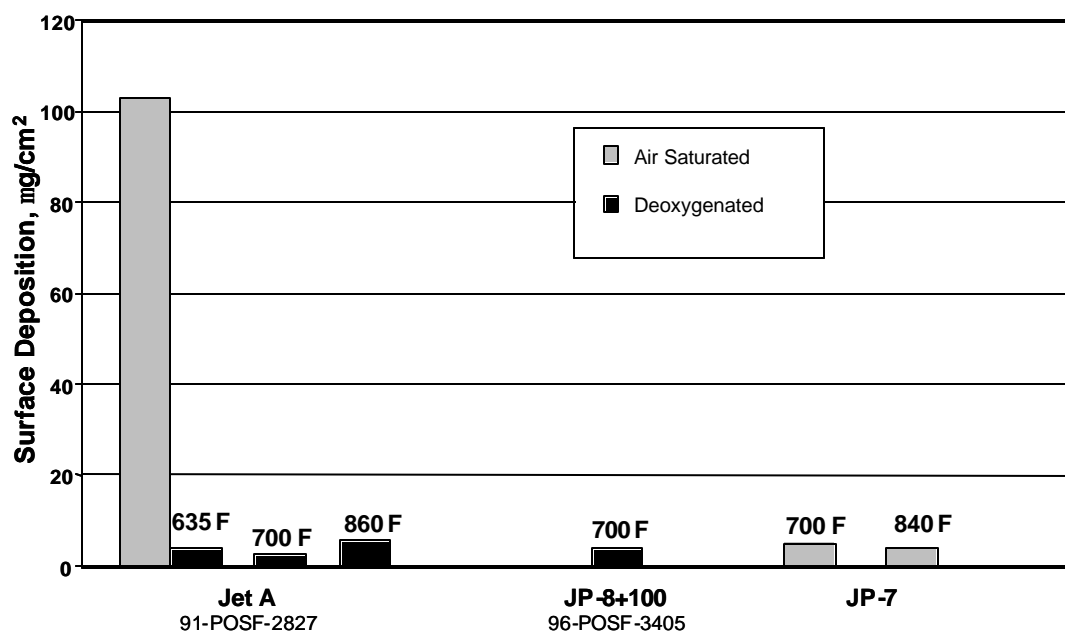
**Figure 8: Deoxygenation Suppresses Coke Formation, Independent of Fuel**

The test conditions and results are summarized in Table 1. They were performed in the order shown (including carbon burn-off), i.e., alternating between air-saturated and deoxygenated fuel. With deoxygenated fuel, there was a dramatic reduction (more than an order of magnitude) in coke deposition on the surface and in particulate suspended in the bulk flow. For the deoxygenated fuel tests, no increase in pressure loss was measured across an in-line test filter located at the exit of the heater tube. Surface deposition results presented in Figure 8 demonstrate that deoxygenation suppresses coke formation, independent of fuel type (cf., Jet A, JP-8, and JP-8+100) or batch (cf., 91-POSF-2827 and 96-POSF-3219). The data in Figure 9 indicate that the deoxygenator is effective in suppressing autothermal reactions up to 860 F peak wall temperatures, confirming the initial hypothesis. Furthermore, deoxygenated Jet A



**Figure 9: Deoxygenation is Effective up to 860 F Peak Wall Temperature**

performed just as well as JP-7, a special high thermal stability fuel that is highly processed and much more costly (see Figure 10). Therefore, it can be inferred that deoxygenation could make possible increasing the maximum allowable temperature of Jet A to that of JP-7, or from 325 F to 550 F, more than doubling the available heat sink. The membrane module was operated for approximately 40 hours with no change in performance. Clearly, additional testing in simulator rigs and engines is required to validate the concept and establish the level of deoxygenation necessary for coke mitigation.



**Figure 10: Deoxygenated Fuel Performs as well as JP-7**

## 5. MODELING

Oxygen permeation rate through a membrane is governed by the fundamental rate equation [9]:

$$\frac{dn_{O_2}(out)}{dt} = \frac{k(\Delta P_{O_2})A}{d} \quad (3)$$

where  $k$  is the oxygen permeability of the membrane,  $\Delta P_{O_2}$  the oxygen partial pressure difference (driving force) across the membrane,  $A$  the membrane surface area,  $d$  the membrane thickness, and  $dn_{O_2}(out)/dt$  the oxygen permeation rate through the membrane. A mechanism-based kinetic model (function of time, temperature, pressure and concentration) for oxygen permeation through the membrane was derived from Eq. 3 and used in conjunction with the test data to estimate the filter size required for a practical (i.e., low-volume/high-flowrate) deoxygenator.

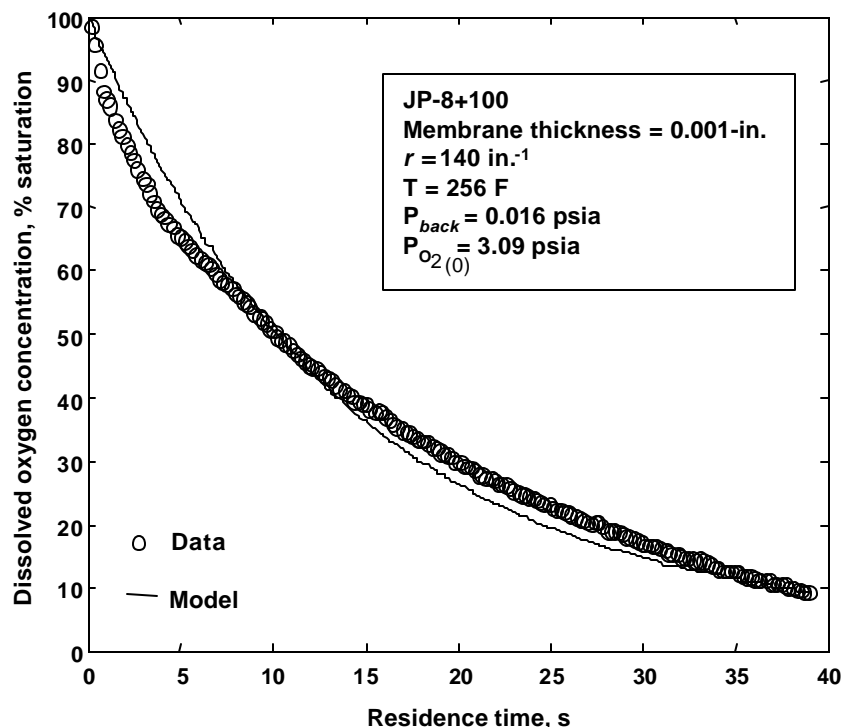
Oxygen removal efficiency ( $\eta_{OR}$ ) is defined as:

$$h_{OR} = 1 - \frac{C_{O_2}}{C_{O_2(0)}} \quad (4)$$

where  $C_{O_2(0)}$  is the initial concentration of oxygen dissolved in jet fuel at ambient conditions, and  $C_{O_2}$  is the final concentration of dissolved oxygen. The oxygen removal efficiency is primarily determined by the partial pressure of oxygen on the backside of the membrane ( $P_{back}$ ), the membrane permeate diffusion coefficient ( $I$ ), the membrane surface-area/volume ratio ( $r$ ), the oxygen mass transfer coefficient ( $f_{MT}$ ), and the residence time ( $t$ ). The performance equation developed from Eq. 3 and 4 is given by:

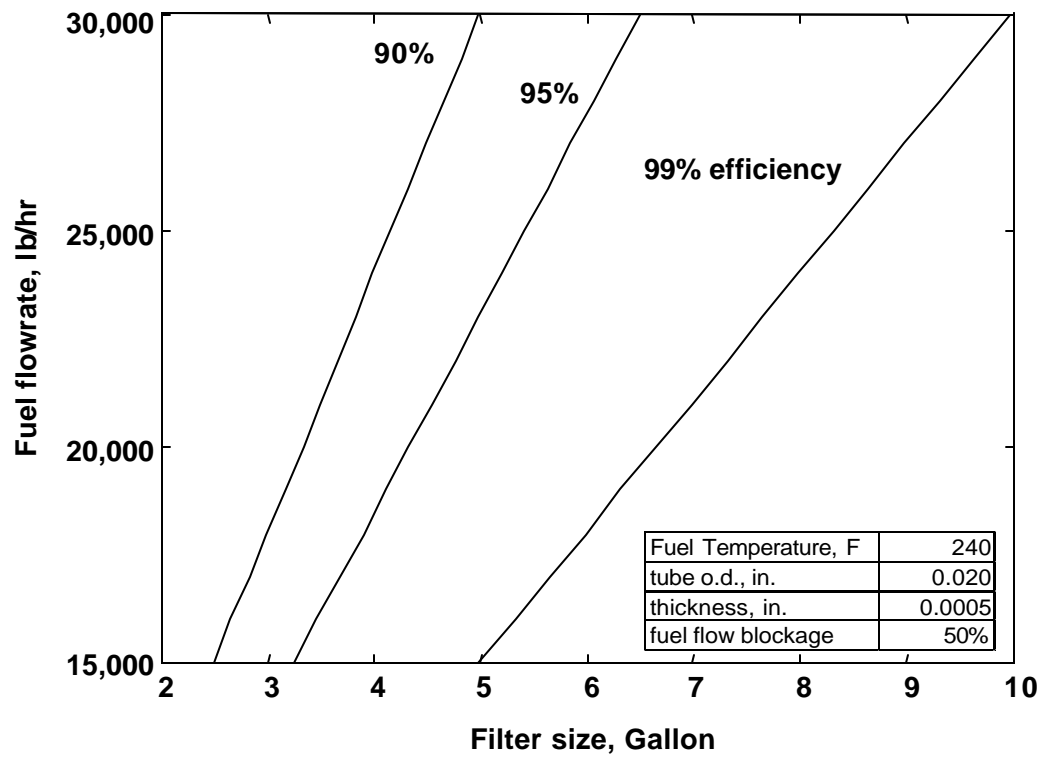
$$h_{OR} = 1 - \left[ \left( 1 - \frac{P_{back}}{P_{O_2(0)}} \right) \cdot \exp\left(-\frac{f_{MT}rI}{g}t\right) + \frac{P_{back}}{P_{O_2(0)}} \right] \quad (5)$$

In this equation,  $P_{back} = 0.21 \cdot P_{vacuum}$ , or 0 for  $N_2$  purge,  $I$  = diffusion coefficient (i.e., permeability/thickness), and  $g = P_{O_2}/C_{O_2}|_{(0)}$  (for Jet A, JP-8, and JP-8+100  $g = 0.0127$ ). The key kinetic parameter, the oxygen diffusion coefficient ( $I$ ) through the membrane is determined from the membrane permeability test data shown in Figure 3. The mass transfer coefficient of oxygen ( $f_{MT}$ ) in liquid fuel is a constant for a particular operating condition and fuel flow configuration. As a demonstration of model validation, a comparative plot of test data against model predictions is illustrated in Figure 11, and shows very good agreement. Under these conditions, the fuel flow was highly turbulent. Therefore, the mass transfer coefficient was assumed to be 1. This assumption was validated experimentally. To develop a more comprehensive design tool, fundamental parameters for estimating the mass transfer coefficient of oxygen in fuel are required.



**Figure 11: Kinetic Model Validation**

The membrane permeation model described by Equation 5 was used as a conceptual design tool. Simulations were carried out to size an on-line fuel deoxygenator for the maximum (~30,000 lb/hr at takeoff) flowrate requirements of a typical commercial aircraft engine, and for different levels of fuel deoxygenation (i.e., 90 to 99%, or 7 to 0.7 ppm). A 50 percent fuel flow (open) area is assumed for the optimum combination of residence time and membrane surface area, corresponding to the minimum component volume. The results, presented in Figure 12, illustrate that a deoxygenator of 10-gallon volume would be adequate, and a smaller volume sufficient if the percentage oxygen removal requirement (efficiency) could be relaxed. Note that the filter size is very dependent on the level to which the fuel must be deoxygenated, since the driving force decreases exponentially as oxygen is removed from the fuel. A determination of the optimum level of fuel deoxygenation was beyond the scope of this study. Alternatively, the deoxygenator might more appropriately be sized for the cruise condition, where engine temperatures are high, fuel flow rate is lower than during acceleration, and flight time is longest.



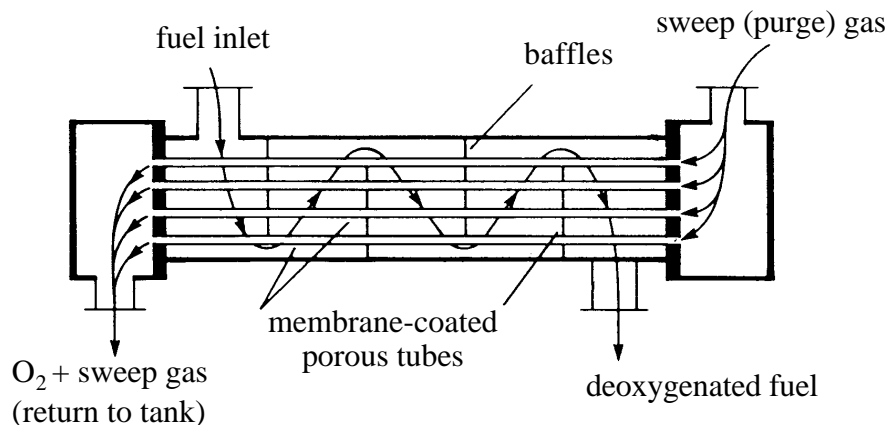
**Figure 12: Fuel Deoxygenation Filter Sizing**

## 6. SYSTEM DESIGN/DEVELOPMENT

The membrane deoxygenator can be configured like a shell-and-tube heat exchanger to maximize the surface area of the membrane contacted by the fuel and minimize the volume of the component. As illustrated in Figure 13, the fuel will flow through the shell, over and around many micro-porous tubes that have been coated on the outside with an ultrathin membrane layer. The inclusion of flow baffles in the shell enhances the diffusion of oxygen to the surface by forcing the fuel to follow a lengthy, tortuous path over the membrane. Dissolved oxygen will permeate into the tubes from the shell, driven by the difference in chemical potential across the membrane.

Control of the oxygen partial pressure on the backside of the membrane can be accomplished by the use of a vacuum pump or by purging with a low flow rate of a gas that does not contain oxygen (a sweep gas). Because no more than 70-ppm oxygen is being removed from the fuel, only a small vacuum pump would be required (less than ¼ HP for a typical commercial aircraft). For operating safety, any fuel (liquid or vapor) that may leak through the membrane will be returned to the fuel storage tank. Alternatively, the sweep gas can be precharged and recirculated in a closed loop, and oxygen transferred from the fuel can be removed by an adsorbent that would be replaced periodically. Also, the pressure of the sweep gas could be controlled to minimize the stress on the membrane.

The next step in the development process is to construct and demonstrate a reduced-scale prototype, and to validate the design and fabrication methodology through extended duration testing in fuel system simulators. A detailed system design/integration and the construction of a full-size component would follow, leading to a final phase to fabricate a full-scale component and demonstrate performance in an engine test.



**Figure 13: Fuel Deoxygenator Design Concept**

## 7. CONCLUSION

The results demonstrate the feasibility of a novel on-line fuel deoxygenation concept, and the potential for improving the fuel thermal-oxidative stability and increasing the cooling capacity. The principal conclusions are:

- On-line removal of dissolved oxygen from jet fuel using a membrane filter is a feasible method for significantly increasing the usable heat sink of the fuel. The results suggest that practical size deoxygenators may be designed for use in aircraft systems.
- Fuel deoxygenation is very effective in suppressing autoxidative coke formation, making it possible to increase the maximum allowable temperature and more than double the available heat sink. The membrane filter is capable of deoxygenating the fuel to a level below that at which significant coking occurs, and should reduce maintenance in aircraft fuel systems.
- The key variables controlling fuel deoxygenation are the difference in oxygen partial pressure across the membrane, the membrane thickness, and oxygen diffusion in the fuel. Thin membranes, operation at elevated temperature, and turbulent flows enhance performance.
- Fuel heating increases the permeability of the membrane and the chemical potential across it.
- The mechanism-based kinetic model for oxygen permeation through a membrane is useful for designing a practical deoxygenator component.



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